Supporting Information for

Robust Chromium Precursors for Catalysis: Isolation and Structure of a Single-Component Ethylene Tetramerization Precatalyst

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General Notes

All synthetic procedures containing chromium were performed in a nitrogen-atmosphere glove box or in sealed containers under a stream of nitrogen gas. All glassware was oven-dried and kept under active vacuum prior to use. Diethyl ether, tetrahydrofuran (THF), toluene, dichloromethane (DCM), hexanes, and pentane solvents were purified by sparging with nitrogen and then passing through a column of activated A2 alumina into sealed containers, degassed under active vacuum and stored over activated molecular sieves prior to use. 1,4-Dioxane was dried over Na/benzophenone, vacuum distilled and kept over activated molecular sieves prior to use. Chlorobenzene was distilled from CaH_2, stored over activated molecular sieves for at least 24 hours, and filtered through activated alumina directly before use. CD_2Cl_2 (Cambridge Isotope Laboratories) was distilled from CaH_2 and kept over activated molecular sieves prior to use. M-MAO 3A was purchased from AkzoNobel as a 7% w/w Al solution in heptane. Ethylene gas was purchased at polymer purity (99.9%) from Matheson, and was dried by passage through two 1L Swagelok steel columns packed with 3Å activated molecular sieves and Mn(II) oxide on vermiculite.[1] $CrCl_3(THF)_3$ was synthesized according to the literature procedure, using $CrCl_3$ (anhydrous) purchased from Strem.[2] The synthesis of ^{iPr}PNP, and $[H(Et_2O)_2][BAr'_4]$ have been previously reported.[3,4] 2-Bromoanisole was purchased from Sigma-Aldrich and distilled before use. The other ether-based aryl bromides were synthesized by methylation or benzylation of the corresponding alcohols, according to the literature procedures,[5-7] and dried under vacuum before use. N-(2-bromobenzyl)-N-ethylethanamine was synthesized as reported.[8] Paramagnetic susceptibility values (μ_{eff}) were determined by NMR (Evans' method).[9,10] Evans' method was performed by dissolving the compound in CD_2Cl_2 solvent (with added protio solvent as the reference). The NMR tube contained a capillary insert with blank CD_2Cl_2:CH_2Cl_2 of the same

composition inside. NMR spectra were recorded on a Varian 300 MHz or 400 MHz Spectrometer. UV/Vis spectra were obtained on a Varian Cary Bio 50 spectrophotometer. EPR spectra were obtained by freezing 1:1 toluene:dichloromethane solutions of [Cr] = 4 mM, using a Bruker EMX spectrometer. Elemental analysis was performed using a PerkinElmer 2400 Series II CHN Elemental Analyzer. Gas chromatography (GC) was performed on an Agilent 6890A instrument using a DB-1 capillary column (10 m length, 0.10 mm diameter, 0.40 μm film) and a flame ionization detector. Gas chromatography/mass spectrometry (GC-MS) was performed on an Agilent 6890A instrument using a HP-5MS column (30 m length, 0.25 mm diameter, 0.50 μm film) and an Agilent 5973N mass-selective EI detector.

X-Ray Crystallography

Suitable crystals of complexes **1**, **2**, **3**, **3′**, **4**, and **5** were mounted on a nylon loop using Paratone oil, then placed on a diffractometer under a nitrogen stream. X-ray intensity data were collected on a Bruker APEXII CCD area detector or a Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS detector employing Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54178 Å) at a temperature of 100 K. All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEX3 software.[11] In APEX3, intensity data were absorption-corrected using SADABS, and space groups were determined on the basis of systematic absences and intensity statistics using XPREP. Using Olex2, the structures were solved using ShelXT and refined to convergence by full-matrix least squares minimization.[12,13] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. In complex **3**, solvent disorder from a combination of 3.4 CH_2Cl_2 and/or pentane molecules (42

electrons each) was treated by SQUEEZE/PLATON. Crystals of complex **3′** were obtained by the same route as complex **3**, but THF was the solvent of crystallization, rather than CH_2Cl_2; the molecular structure is shown in Figure S1. In complex **3′**, the disorder in the ethereal ligand bound to Cr was modeled as a mixture of THF and 1,4-dioxane using the PART instruction (1,4-dioxane was also used in the synthetic protocol) and C-C bond distance constraints and restraints. For complex **5**, the disorder in five of the eight CF_3 groups of the BAr'_4 anion was modeled using the PART instruction and bond distance and anisotropic displacement parameter restraints. In complex **5**, the CH_2Cl_2 solvent disorder was modeled using the EQIV instruction, placing half of a molecule of CH_2Cl_2 in the asymmetric unit. Graphical representation of structures with 50% probability thermal ellipsoids were generated using Diamond 3 visualization software.[14]

Table S1. Crystal and Refinement Data for Complexes **1** and **2**.

Compound	**1**	**2**
CCDC	1895679	1895680
Empirical formula	$C_{42}H_{39}CrO_3$	$C_{45}H_{45}CrO_3$
Formula weight	643.73	685.81
Temperature/K	99.97	99.99
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	10.7286(4)	11.5802(10)
b/Å	11.7519(4)	15.8845(12)
c/Å	15.0753(5)	20.0281(17)
α/°	95.481(2)	90
β/°	102.260(2)	103.123(3)
γ/°	115.318(2)	90
Volume/$Å^3$	1641.19(11)	3587.9(5)
Z	2	4
$\rho_{calc}g/cm^3$	1.303	1.270
μ/mm^{-1}	3.170	0.359
F(000)	678	1452
Crystal size/mm^3	0.166 × 0.14 × 0.086	0.314 × 0.245 × 0.22
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.14 to 136.72	4.902 to 72.626
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-18 \le l \le 18$	$-19 \le h \le 19$, $-26 \le k \le 26$, $-33 \le l \le 33$
Reflections collected	44667	210362
Independent reflections	6047 [R_{int} = 0.0679, R_{sigma} = 0.0454]	17385 [R_{int} = 0.0701, R_{sigma} = 0.0305]
Data/restraints/parameters	6047/0/415	17385/0/442
Goodness-of-fit on F^2	1.041	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0493, wR_2 = 0.0983	R_1 = 0.0409, wR_2 = 0.1106
Final R indexes [all data]	R_1 = 0.0685, wR_2 = 0.1061	R_1 = 0.0594, wR_2 = 0.1225
Largest diff. peak/hole / e $Å^{-3}$	0.300/-0.472	0.703/-0.619

Table S2. Crystal and Refinement Data for Complexes **3** and **3′**.

Compound	**3**	**3′**
CCDC	1895681	1895682
Empirical formula	$C_{21}H_{21}CrO_3$	$C_{25}H_{29}CrO_{4.58}$
Formula weight	373.38	454.80
Temperature/K	100.0	100.05
Crystal system	triclinic	monoclinic
Space group	P-1	Cc
a/Å	12.0150(16)	20.0935(10)
b/Å	12.4851(16)	11.1921(6)
c/Å	15.1703(19)	10.9889(5)
α/°	75.513(5)	90
β/°	87.541(5)	116.859(2)
γ/°	80.203(5)	90
Volume/Å^3	2171.2(5)	2204.68(19)
Z	4	4
ρ_{calc}g/cm^3	1.142	1.370
μ/mm^{-1}	0.540	0.551
F(000)	780	959
Crystal size/mm^3	0.252 × 0.179 × 0.125	0.406 × 0.168 × 0.108
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.42 to 66.342	6.650 to 72.734
Index ranges	-17 ≤ h ≤ 18, -19 ≤ k ≤ 19, -23 ≤ l ≤ 22	-33 ≤ h ≤ 33, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18
Reflections collected	102156	60629
Independent reflections	14945 [R_{int} = 0.0687, R_{sigma} = 0.0569]	10655 [R_{int} = 0.0585, R_{sigma} = 0.0405]
Data/restraints/parameters	14945/0/457	10655/10/320
Goodness-of-fit on F^2	1.039	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0610, wR_2 = 0.1147	R_1 = 0.0310, wR_2 = 0.0730
Final R indexes [all data]	R_1 = 0.0897, wR_2 = 0.1247	R_1 = 0.0366, wR_2 = 0.0750
Largest diff. peak/hole / e Å^{-3}	0.696/-0.613	0.667/-0.493

Table S3. Crystal and Refinement Data for Complexes **4** and **5**.

Compound	**4**	**5**
CCDC	1895683	1895684
Empirical formula	$C_{27}H_{33}CrO_3$	$C_{77.5}H_{62}BClCrF_{24}NO_2P_2$
Formula weight	457.53	1655.48
Temperature/K	100.09	100.01
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P-1
a/Å	8.3974(4)	12.9268(7)
b/Å	22.6187(10)	16.7595(10)
c/Å	12.1007(5)	18.9950(9)
α/°	90	104.445(2)
β/°	92.754(2)	96.510(2)
γ/°	90	107.746(2)
Volume/Å^3	2295.73(18)	3714.6(4)
Z	4	2
ρ_{calc}g/cm^3	1.324	1.48
μ/mm^{-1}	0.524	0.341
F(000)	972	1684
Crystal size/mm^3	0.198 × 0.143 × 0.133	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.778 to 72.716	4.526 to 67.496
Index ranges	-13 ≤ h ≤ 13, -37≤ k ≤ 37, -19 ≤ l ≤ 20	-20 ≤ h ≤ 20, -26 ≤ k ≤ 25, -29 ≤ l ≤ 29
Reflections collected	87691	199425
Independent reflections	11083 [R_{int} = 0.0548, R_{sigma} = 0.0363]	29673 [R_{int} = 0.0508, R_{sigma} = 0.0379]
Data/restraints/parameters	11083/0/283	29673/369/1135
Goodness-of-fit on F^2	1.065	1.100
Final R indexes [I>=2σ (I)]	R_1 = 0.0444, wR_2 = 0.0987	R_1 = 0.0621, wR_2 = 0.1413
Final R indexes [all data]	R_1 = 0.0631, wR_2 = 0.1056	R_1 = 0.0808, wR_2 = 0.1500
Largest diff. peak/hole / e Å^{-3}	1.357/-0.488	1.197/-2.170

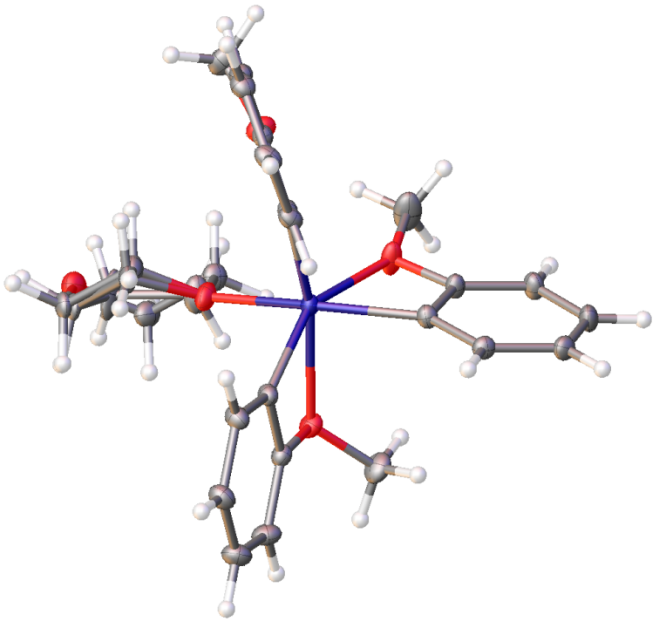

Figure S1. Solid-state structure of complex **3′**, which is obtained by following the synthetic protocol for **3**, yet growing crystals in THF. The coordinated ethereal ligand is modeled as a mixture of THF/1,4-dioxane (1,4-dioxane is used in the synthesis of **3/3′**).

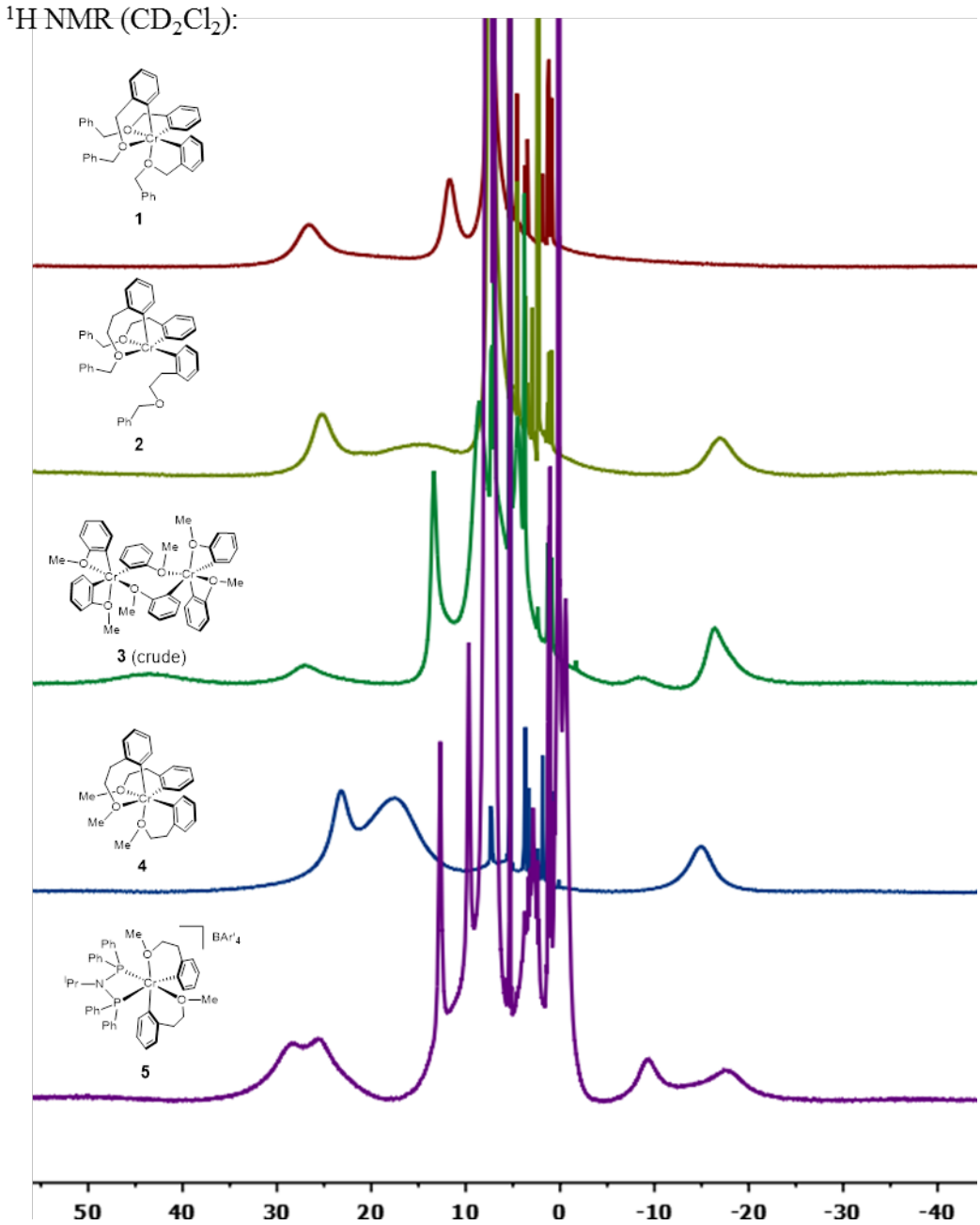

Figure S2. Paramagnetic ^{1}H NMR spectra. Each sample is prepared in CD_2Cl_2 with [Cr] ≈ 100 mM.

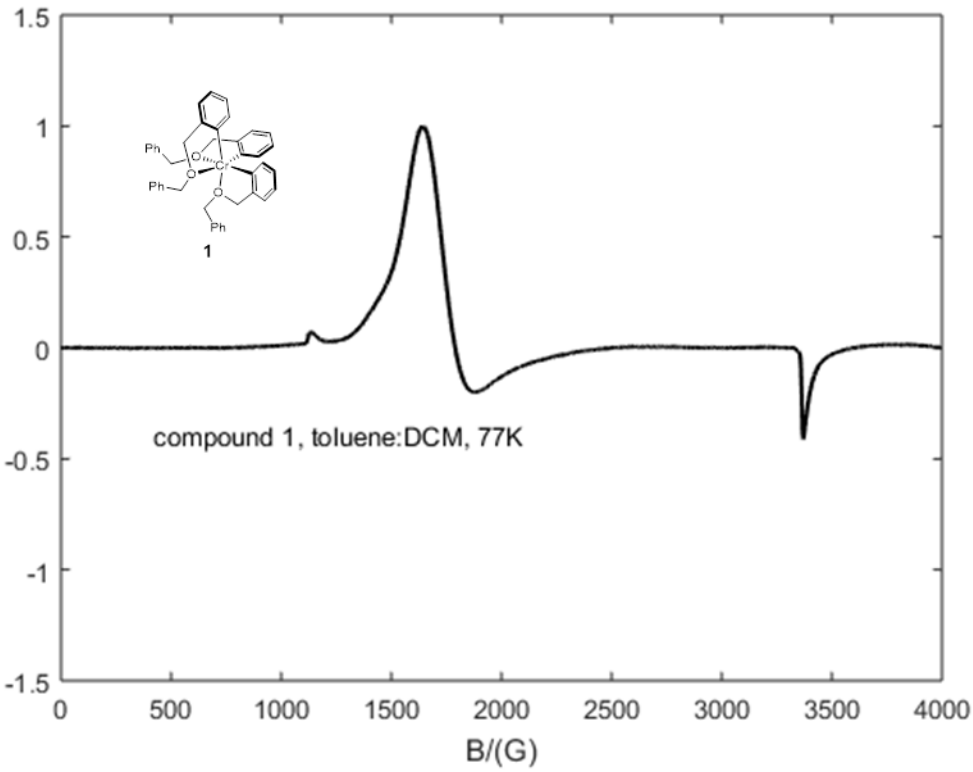

Figure S3. Continuous wave (cw) EPR spectrum of compound **1**. Temperature: 77K. Microwave frequency: 9.4 GHz. Microwave power: 6.4 mW. Modulation frequency: 100 kHz. Modulation amplitude: 4.0 G.

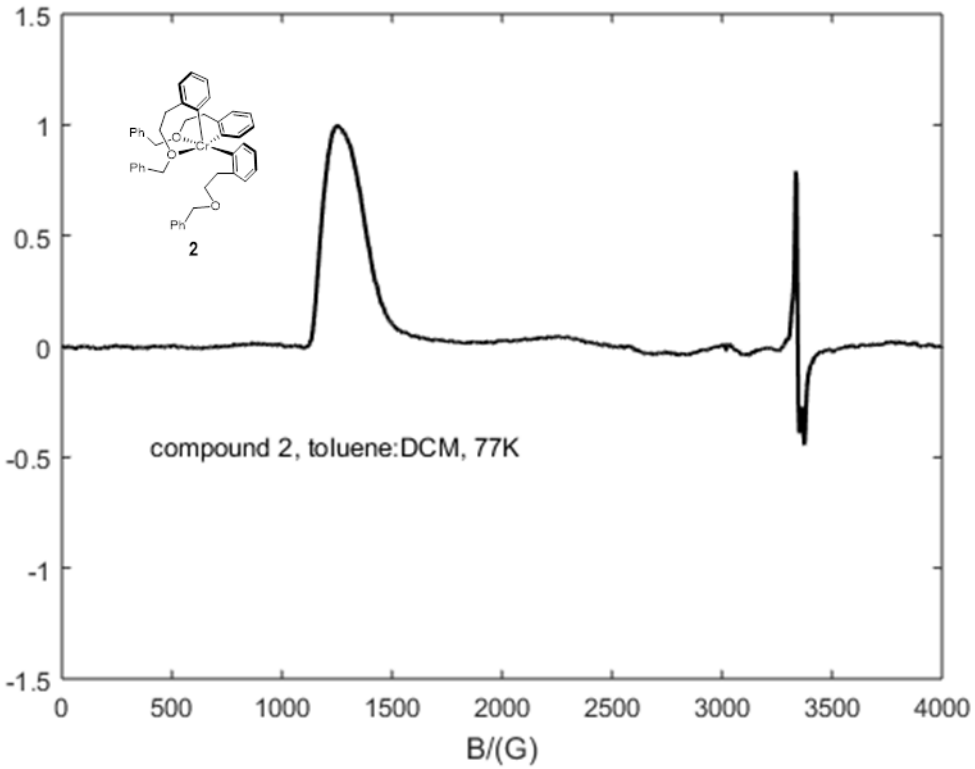

Figure S4. Continuous wave (cw) EPR spectrum of compound **2**. Temperature: 77K. Microwave frequency: 9.4 GHz. Microwave power: 6.4 mW. Modulation frequency: 100 kHz. Modulation amplitude: 4.0 G.

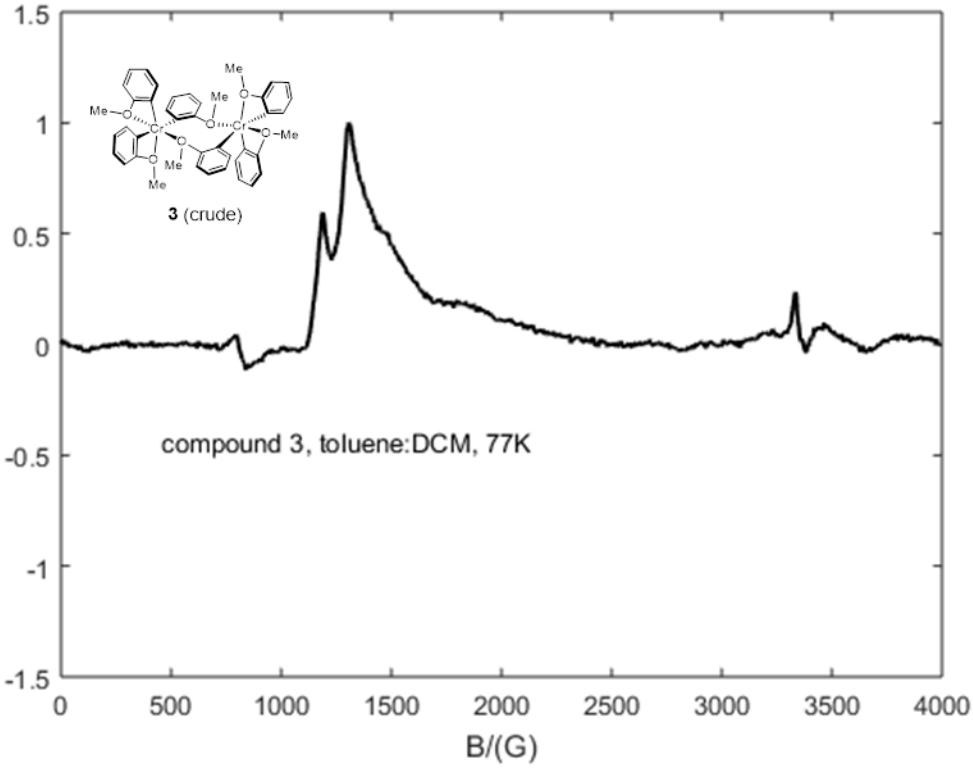

Figure S5. Continuous wave (cw) EPR spectrum of compound **3**. Temperature: 77K. Microwave frequency: 9.4 GHz. Microwave power: 6.4 mW. Modulation frequency: 100 kHz. Modulation amplitude: 4.0 G.

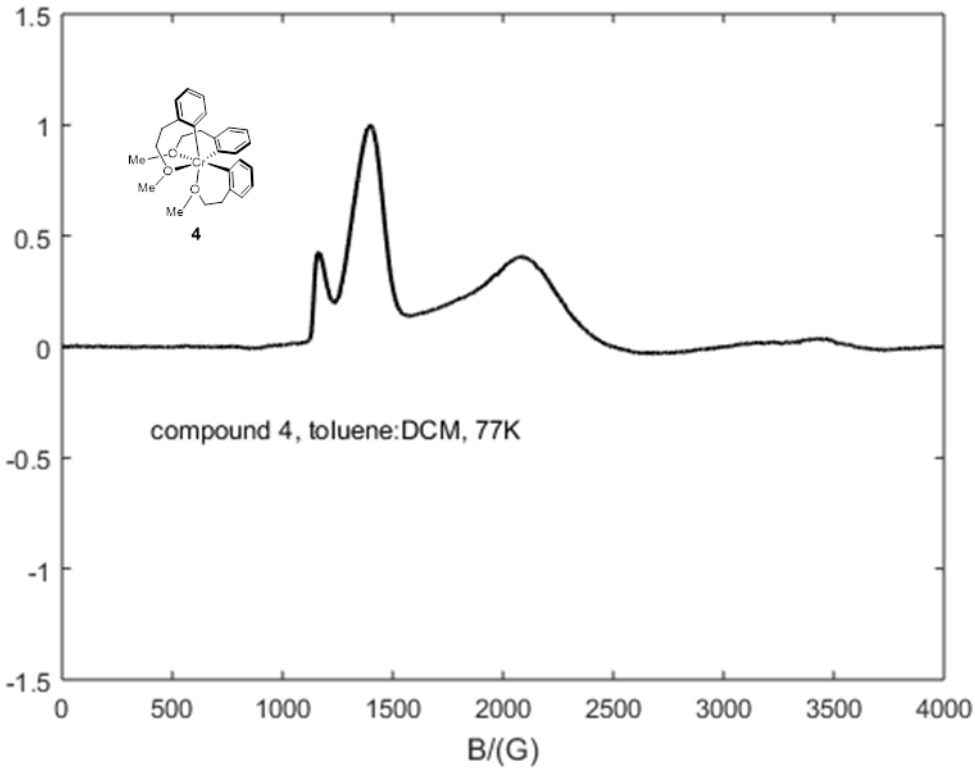

Figure S6. Continuous wave (cw) EPR spectrum of compound **4**. Temperature: 77K. Microwave frequency: 9.4 GHz. Microwave power: 6.4 mW. Modulation frequency: 100 kHz. Modulation amplitude: 4.0 G.

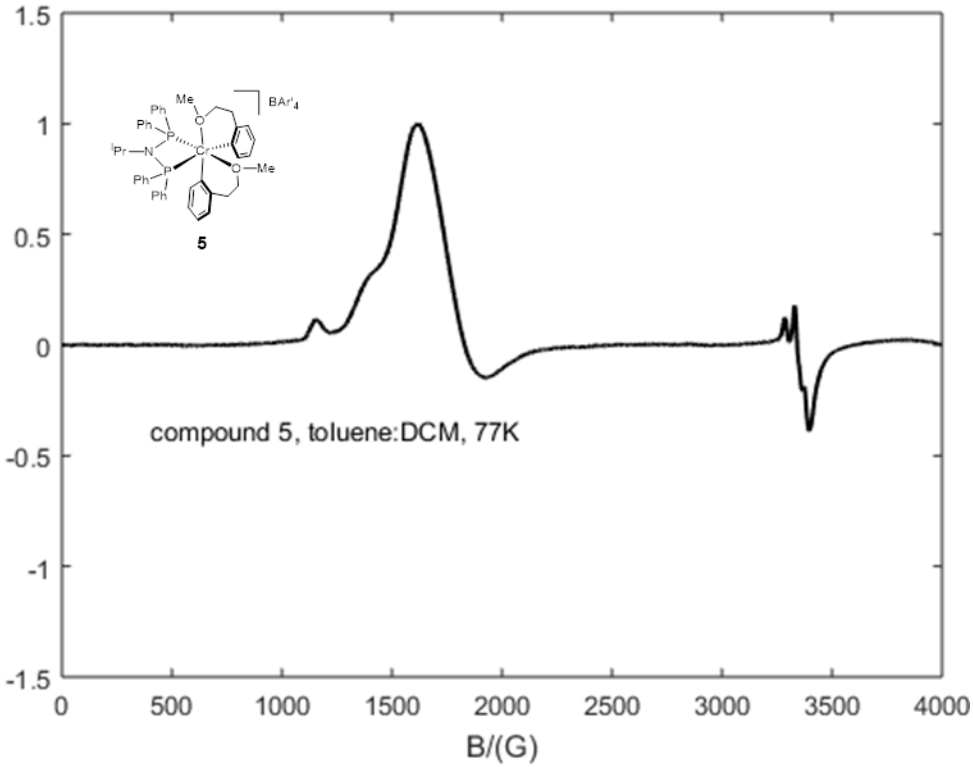

Figure S7. Continuous wave (cw) EPR spectrum of compound **5**. Temperature: 77K. Microwave frequency: 9.4 GHz. Microwave power: 6.4 mW. Modulation frequency: 100 kHz. Modulation amplitude: 4.0 G.

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